TUNABLE INTERFACES IN FIBER REINFORCED-POLYMER COMPOSITES USING PLASMA SURFACE TREATMENTS

Jacqueline H. Yim*, Alexander Fridman, Giuseppe R. Palmese
Department of Chemical & Biological Engineering
A.J. Drexel Plasma Institute
Drexel University
Philadelphia, PA, 19104

D. Daphne Pappas
U.S. Army Research Laboratory,
Aberdeen Proving Ground, MD, 21005

Denis Kissounko
Center for Composite Materials – University of Delaware
Newark, DE 19711

ABSTRACT

Fibers incorporated into polymer matrices suffer from poor adhesion at the fiber-resin interface. In ballistic materials such as body armor, it is imperative that the fiber-resin interface is strengthened for superior energy absorbing capabilities. To address this need, fibers are typically subjected to surface modifications. The overall aim of this work is to establish a methodology of controlling the interfacial adhesion by controlling the degree of chemical bonding between the fiber and the resin. In this study, plasma surface treatments were applied to ultra high molecular weight polyethylene (UHMW-PE) fibers to introduce chemical functionalities to promote covalent bonding. Nitrogen and oxygen plasmas were used and changes imposed by the plasma were characterized using surface analytical techniques. The adhesional strength and energy absorption of the plasma-modified fibers/epoxy interface were assessed using a single-fiber microdroplet shear test. FTIR and XPS reveal the existence of four main chemical groups – hydroxyl, carboxylic, carbonyl and amine groups. Characterization of the interface showed that a six-fold increase of the interfacial shear strength (IFSS) can be attained from plasma treating the fibers.

1. INTRODUCTION

Fiber-reinforced polymer composites have been the material of choice in lightweight ballistic applications owing to their exceptional mechanical properties and stress-transfer capabilities. The stiffness and strength of the composite is dependent upon the mechanical properties of the individual components whereas the stress-transfer properties are governed by the interactions at the fiber-matrix interface. However, the overall performance of these materials is limited by the weak interfacial adhesion between the organic fibers and the polymer matrix as a result of the fibers' low surface energy, chemical inertness, and poor wettability. To correct this problem, surface treatments have been utilized to alter the surfaces' of fibers through the introduction of chemical reactive groups and/or by surface roughening to promote mechanical interlocking. By incorporating specific reactive groups, a higher degree of covalent bonding between the fiber and resins such as vinyl ester and epoxy can significantly increase the adhesion strength. Over the past decade, low-temperature plasma treatments have gained popularity over conventional wet-chemical and mechanical techniques. It was reported that an increase of 40% in adhesional strength was achieved through the use of low-pressure plasma surface treatments (Holmes, 1990). Although low-pressure systems are effective, the use of costly vacuum systems have deterred large-scale use thus atmospheric systems have been sought as a viable alternative. Atmospheric pressure plasma treatments have shown to effectively impart functional groups, modify only the top monolayers while preserving the bulk material properties, avert thermal degradation of the polymer while providing a quick, tunable and economical process. From a throughput standpoint, developing surface treatment methodologies based on model systems can serve as a basis for scale-up processes that would prove to be practical for the manufacturing of composite panel structures.

Plasma is a weakly ionized gas where the gas is dissociated into electrons, ions, free radicals, excited species and metastables when an electric field is applied. The electrons and UV generated in the plasma aid in the breaking of bonds at the polymer backbone whereas the free radicals, energetic species, metastables, in addition to the electrons and ions play an important role in the plasma chemistry processes such as ionization, recombination, attachment, etc. Plasma-polymer interactions that have been observed include (i) surface cleaning, (ii) etching, (iii) crosslinking, or (iv) modification of the surface chemistry and depending upon the treatment conditions, reactor design, and gas chemistry applied, the effects can be synergistic (Liston, 1993).

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Work presented here focuses on establishing the efficacy of using atmospheric low-temperature plasma treatments in modifying the surfaces of ultra-high molecular weight polyethylene fibers to where significant improvement in adhesion can be achieved. By implementing different treatment conditions such as treatment time and gas flow-rate, the level of chemical functionalization can be controlled and hence the degree of chemical bonding of the fiber to the resin can be controlled. In doing so, we can develop an operating window of parameters that can be established between plasma treatment conditions and functionalization. This will be able to provide us with the groundwork to link the degree of surface activation to adhesion properties in model systems.

2. EXPERIMENTAL

2.1 Material Preparation

Prior to plasma treatments, ultra high molecular weight polyethylene (UHMWPE) fibers (20 μm in diameter) were washed in distilled water heated to 90°C for 2 hours. The fibers were then removed and dried in an oven at 60°C for 2 hours. The cleaning process is essential as to ensure that any residual fiber finish or weaving aid used during web formation is removed.

2.2 Plasma Treatments

Plasma treatments were carried out in a customized, planar dielectric barrier discharge (DBD) reactor system equipped with a microsecond-pulsed power supply. The schematic diagram of the DBD plasma reactor is shown in Figure 1. The reactor has the capability to treat substrates with dimensions of up to 6"x 6" and thicknesses not exceeding 2 mm. The reactor consists of two 6" x 6" stainless steel electrodes and a quartz dielectric that sit on top of the high voltage electrode. The microsecond-pulsed power supply was applied to generate the plasma between the top electrode and the quartz within a gap distance of 2 mm.
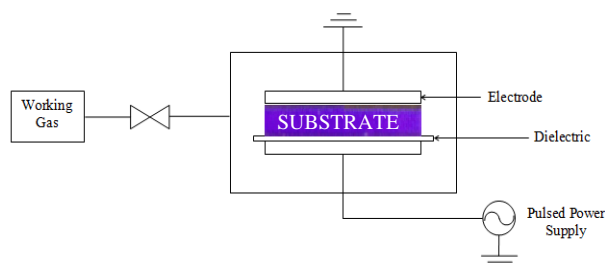

Figure 1. Schematic of Pulsed-Dielectric Barrier Discharge Plasma Reactor

The power supply is designed so that high-voltage pulses with a rise time on the order of microseconds are delivered to the reactor. The intent behind the microsecond pulses is to emulate the type of discharge

that one would obtain if using a low-pressure plasma system. The principle underlying this effect can be found in (Fridman, 2005). Treatments varied based on the gas used to initiate the plasma, gas flow-rate, and exposure time. Gases used in this study are ultra-high purity nitrogen and oxygen and they were administered into the reactor using a digital mass flow controller with flow-rates ranging from 1-10 standard liter s per minute (SLPM). Modifications incurred to the UHMW-PE woven fabric are limited to one side as they were mounted flat onto the quartz-covered electrode as the plasma was formed in the gap.

2.3 Surface Analysis

Attenuated total reflectance – Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS) were utilized to identify chemical groups formed on the surface of the plasma-treated UHMW-PE fabrics. ATR-FTIR analysis was performed using a Nicolet-Thermo 670 FTIR equipped with a Specac® Silver-Gate single reflection zinc selenide (ZnSe) ATR attachment purged with nitrogen. Spectra were recorded using a mercury-cadmium-telluride (MCT) detector at a resolution setting of 4 cm^{-1} with a total of 164 scans. Near surface compositional depth profiling was performed using the Kratos Axis Ultra 165 X-ray photoelectron spectroscopy (XPS) system, equipped with a hemispherical analyzer. A 100 W monochromatic Al Kα (1486.7 eV) beam irradiated a 1 mm x 0.5 mm sampling area and the take-off angle was 90°. Elemental high resolution scans for C1s, O1s, and N1s were taken at the pass energy of 20 eV. Deconvolution of high resolution peaks was done using the CasaXPS processing software (Casa Software Ltd, UK).

2.4 Interfacial Shear Stress Testing

To characterize the bonding behavior of the fiber to resin at the interface, a data reduction scheme referred to as the single-fiber microdroplet pull out test was utilized. This technique is described in detail in (Gao, 2008). The apparatus used to measure the interfacial shear stress and energy absorption is shown in Figure 2.
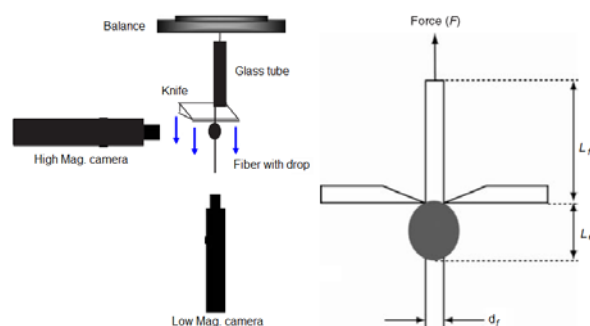

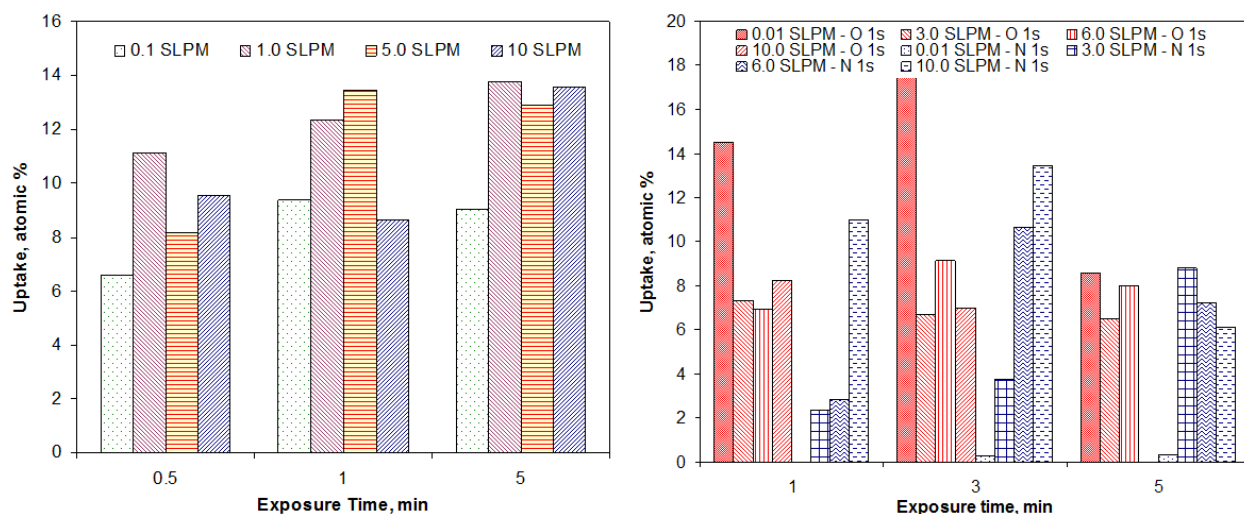Figure 2. Schematic single-fiber microdroplet pull out test setup

Figure 3. Atomic concentration (%) of oxygen groups from oxygen plasma (left) and oxygen and nitrogen from nitrogen plasma (right).

The resin used for the tests is an amine cured epoxy system. The resin drop is comprised of a low viscosity diglycidyl ether of bisphenol A epoxy resin (Dow Chemical Company DER 353) mixed with the curing agent, bis(*p*-aminocyclohexyl) methane (Air Products and Chemical, PACM) at stoichiometric ratios of 100:28. The epoxy droplets were allowed to gel at room temperature for 6 h followed by a post cure at 80°C for 2h and 150°C for another 2 h. A total of three microdroplet samples were tested per plasma-treated fibers. Inaccuracies arising from (1) the displacement of the droplet, (2) increase of the fiber length due to stretching, and (3) the deformation of the test apparatus have been taken into consideration in order to minimize the error in IFSS measurements.

3. RESULTS & DISCUSSION

3.1 Chemical Analysis

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS) analyses confirm the formation of nitrogen and oxygen-containing groups. A key observation of the surface treatment is that at longer exposure times and higher oxygen and nitrogen gas flow-rates, the concentration of oxygen-containing groups and nitrogen-containing groups increases, respectively as shown in Figure 3.

Deconvolution of high resolution C1s peaks provided insight into the various chemical groups formed on the surface. These groups consisted of hydroxyl (-OH), carboxylic (-COOH), carbonyl (-C=O), and amine (-C-N) groups at binding energies of 286.5, 289.5, 288.0, and 285.8 eV as seen in Figure 4.
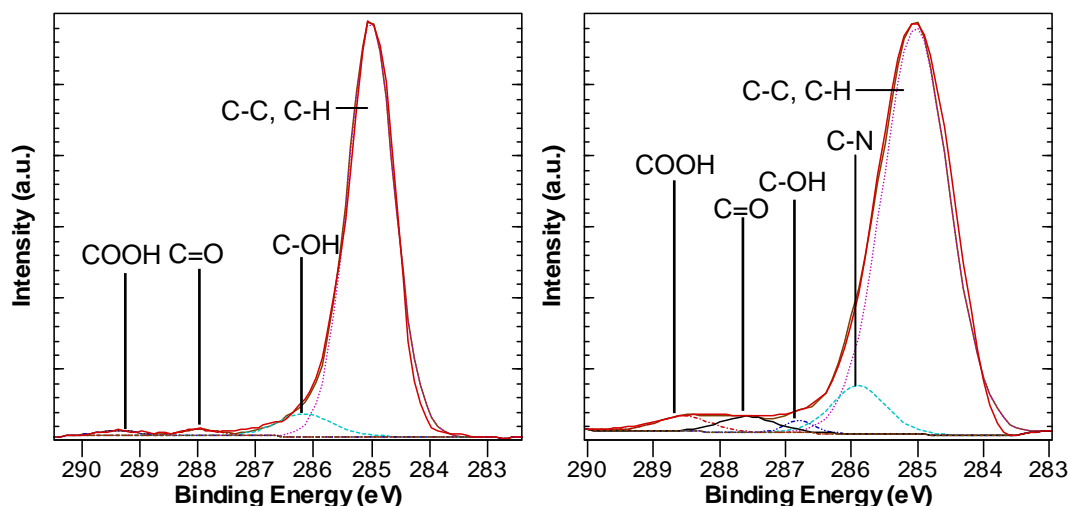

Figure 4. Deconvolution of C1s peaks obtained for UHMW-PE fibers treated under oxygen plasma for 3 minute (left) and nitrogen plasma for 3 minutes (right)

Table 1. Relative fraction (%) of chemical functionalities obtained from HR C1s of N_2 and O_2 plasma-treated fibers

Treatment Conditions			Relative area corresponding to chemical groups (%)				
Plasma	Flow-rate (SLPM)	Exposure time (min)	C-C, C-H 285.0 eV	-C-OH 286.5 eV	-COOH 289.5 eV	-C-N 285.8 eV	-C=O 288.0 eV
	control		100.0				
N_2	1	1	85.74	7.25	5.13	0	1.88
N_2	1	3	81.62	3.61	2.02	0	0
N_2	10	1	66.38	23.23	3.66	4.39	2.35
N_2	10	3	69.91	12.35	6.91	6.38	4.45
O_2	5	1	93.57	3.69	1.19	0	1.54
O_2	5	3	77.47	12.26	7.09	0	3.19
O_2	10	1	61.43	25.90	9.05	0	3.63
O_2	10	3	73.03	13.88	4.97	0	8.11

A comparison looking at the relative concentration or the area under each fitted component peaks was performed, as summarized in Table 1, in order to see if processing conditions played a substantial role in the formation of these reactive groups.

From this comparison, there is a difference in the concentration of the chemical groups based upon the exposure time and gas flow-rates utilized during treatments. In some instances, in the case of the fibers treated under nitrogen plasma at a flow-rate of 10 SLPM, the concentration of hydroxyl groups significantly drops while the concentration of the carboxylic, nitrogen, and carbonyl groups increases with longer exposure time. Similar trends are also observed on fibers treated in oxygen plasma. We believed that the chemical processes that take place at the surface of the substrate and in the plasma can provide valuable insight into how these chemical groups are formed.

3.2 Interfacial Properties

Interfacial Shear Strength (IFSS)

The average interfacial shear strength (IFSS) measured at the fiber-epoxy interface was calculated using a simple analytical approach from the following relationship:

$$IFSS = \frac{F_c}{A} = \frac{F_c}{\pi d_f l_e} \qquad (1)$$

where F_c is the maximum force for the load-displacement curve, shown in Figure 5, d_f is the fiber diameter, and l_e is the embedded microdroplet length. IFSS values for the plasma treated fibers are summarized in Table 2. Figure 6 is a SEM micrograph of a control and plasma-treated single fiber of UHMW-PE prepared for testing.
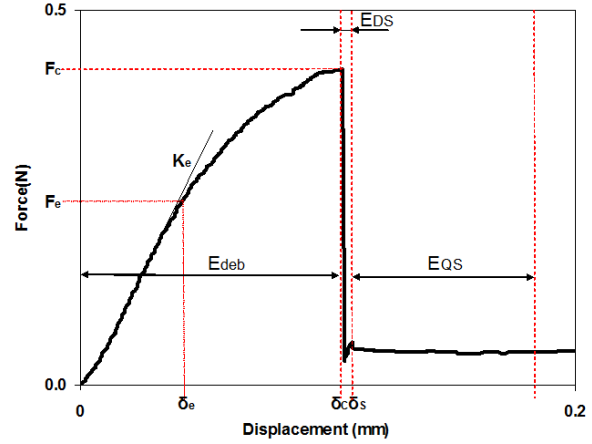

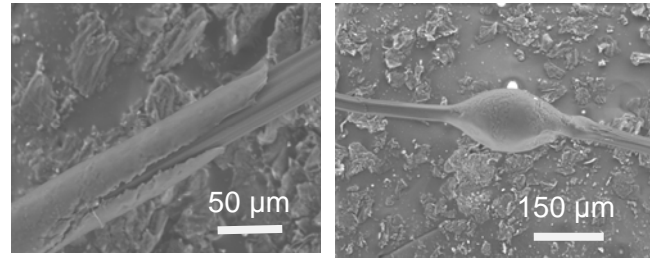Figure 5. Representative example of load-displacement curve

Figure 6. SEM images of single fibers with epoxy microdroplet on an untreated (top) and plasma-treated (bottom) samples.

The control sample exhibited low interfacial shear strength due to the lack of chemical bonding of the fiber to the epoxy. In the plasma-treated fibers, significantly higher values of interfacial shear strength were recorded, predominantly because of the available reactive sites providing covalent bonds. Overall, from these microdroplet tests, the plasma-modified fibers exhibited a two- to six-fold increase in IFSS compared to that of the control sample.

Table 2. Calculated IFSS and energy absorption measurements obtained from microdroplet testing

Sample No.	Plasma	Flow-rate, SLPM	Exposure time, min	IFSS, MPa	E^{sp}_{deb}, kJ/m²	E^{sp}_{ds}, MJ/m²	E^{qs}_{deb}, MJ/m²
control	-	-	-	2.04±1.1	0.05±0.01	1.26±1.0	0.66±0.2
1	N₂	1	1	8.25±1.8	0.78±0.2	8.88±1.8	0.43±0.2
2	N₂	10	1	5.54±1.5	0.81±0.2	5.62±1.5	3.52±1.3
3	N₂	10	3	11.74±2.1	0.14±0.1	14.57±2.1	1.05±0.5
4	O₂	10	3	9.51±1.9	0.90±0.2	13.62±1.9	4.98±1.4
5	O₂	1	1	8.69±2.1	0.25±0.1	13.25±2.2	1.53±1.0
6	O₂	10	1	9.17±2.0	0.34±0.1	4.23±1.1	4.02±1.3

However, based on these results it is difficult to assess whether the improved adhesional property exhibited from the plasma-treated fibers was achieved from a specific reactive group.

Energy Absorption (E)

From the microdroplet tests, energy absorption properties were also measured. Energy absorption (E) is broken into three components due to different stages arising from failure: energy absorption due to debonding (E_{deb}), energy absorption due to dynamic sliding (E_{ds}), and energy absorption due to quasi-static sliding (E_{qs}). The energy absorption due to debonding, dynamic sliding, and quasi-static sliding is defined in the following (Gao, 2008):

$$E^{sp}_{deb} = \frac{E_{a,deb}}{A} \qquad (2)$$

$$E^{sp}_{ds} = \frac{E_{a,ds}}{(\Delta L_f + \Delta \delta_f)A} \qquad (3)$$

$$E^{sp}_{qs} = \frac{E_{a,qs}}{l_e A} \qquad (4)$$

where ΔL_f and $\Delta \delta_f$ is the fiber stretching length and the displace change when the force drops from F_c to F_s in the dynamic sliding region. The fiber stretching length can be calculated using (Gao, 2008):

$$\Delta L_f = \frac{4000 \times (F_c - F_s) \times l_f}{\pi d_f^2 E_f} \qquad (5)$$

where the E_f is the Young's modulus of the UHMW-PE fiber.

In general, the energy absorption of the plasma treated fiber is higher than that of the untreated fiber. The frictional sliding contributions to energy absorption are observed where the resin is at the onset or beginning stages of debonding from the fiber. The influence of covalent bonding from the reactive groups interacting with the resin can be taken into account based on the calculated energy absorption values due to debonding and dynamic sliding. Energy absorption due to quasi-static is much less pronounced than that due to dynamic sliding. This is believed to be attributed to the low level of surface roughness (mechanical interlocking) at the interface of the fiber and the resin. Overall, the information obtained from the microdroplet test demonstrates that fibers modified with plasma exhibit higher strength and increased energy absorbing characteristics.

CONCLUSIONS

Atmospheric pressure plasma treatments have shown to be a valuable tool in creating reactive chemical groups on the surfaces of chemically inert organic fibers. Attenuated total reflectance-Fourier Transform Spectroscopy (ATR-FTIR), X-ray Spectroscopy (XPS) and interlaminar shear strength (ILSS) tests reveal that the adhesional properties can be improved significantly through the initiation of covalent bonds. It has been shown that the critical parameters such as the gas flow-rate and exposure time affect the degree of functionalization. By using the microdroplet tests on a single fiber, the interfacial shear strength as well as the absorbed energies due to debonding, dynamic sliding, and quasi-static sliding have been quantified and a considerable increase in the interlaminar shear strength from 2.04 ± 1.1 MPa to as high as 11.74 ± 2.1 MPa have been achieved. These results are important as they signify that the use of plasma treatments with optimized conditions can provide a means of controlling the interfacial strength between the fibers and polymer matrices.

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